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Abstract
Model chemistries that employ additivity schemes have become increasingly popular within the chemical community. These approaches are predicated upon the assumption that less rigorous (and, therefore, less expensive) calculations may be combined to approximate a more accurate (and otherwise intractable) level of theory. Most of these models make some use of an empirical correction, the desirability of which is at best questionable. The present paper critically examines the importance of one such correction (the "higher-level correction") to the most widely used additivity method (the Gaussian model). An alternative approach, which does not depend upon any sort of *ad hoc* empiricism, is also outlined. The current model is found to offer accuracy comparable to that of the Gaussian model.

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On the question of empirical corrections in *ab initio* model chemistries

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Model chemistries that employ additivity schemes have become increasingly popular within the chemical community. These approaches are predicated upon the assumption that less rigorous (and, therefore, less expensive) calculations may be combined to approximate a more accurate (and otherwise intractable) level of theory. Most of these models make some use of an empirical correction, the desirability of which is at best questionable. The present paper critically examines the importance of one such correction (the ''higher-level correction'') to the most widely used additivity method (the Gaussian model). An alternative approach, which does not depend upon any sort of *ad hoc* empiricism, is also outlined. The current model is found to offer accuracy comparable to that of the Gaussian model. © *1999 American Institute of Physics.* [S0021-9606(99)31013-8]

The accurate prediction of thermochemistry continues to be an important goal of computational chemistry. While certain quantities (e.g., proton affinities) are amenable to relatively modest levels of theory, others (e.g., dissociation energies) often require substantially more computational effort. A great deal of work has, therefore, been directed toward the development of efficient theoretical methods.

The most popular approaches have come to be known collectively as the ''Gaussian'' model,[1] the G2 method and its derivatives having proved very successful in reproducing a variety of experimental values. These techniques are based upon additivity schemes whereby a series of computationally less demanding calculations are combined so as to approximate a more rigorous level of theory.[2]

While the Gaussian model is predicated upon an *ab initio* approach, an empiricism is, nevertheless, introduced, the so-called ''higher-level correction'' (HLC). This empirical correction has consisted of two parameters: one to insure a correct absolute energy for the hydrogen atom, and the other to minimize the deviation between calculated and experimental values.[3] The HLC itself is expressed in terms of the number of alpha and beta valence electrons. The use of empirical corrections in model chemistries raises a number of questions. For example: How applicable are such models to chemical species far removed from those used in the statistical fits? Does the inclusion of empirical corrections obscure the underlying physics of the systems under study? Nonetheless, the G2 methods have provided very useful predictions of thermodynamic quantities. The research reported in this paper was undertaken to assess the importance of empirical corrections in first-principle model chemistries and to consider alternatives to the current G2 approach.

Curtiss *et al.*[1(c)] have proffered a set of 125 thermochemical quantities, all with well established experimental values, as a benchmark for theory. This test set consists of fifty-five dissociation energies (D_e), thirty-eight ionization potentials (IP), twenty-five electron affinities (EA), and seven proton affinities (PA). The G2 method reproduces these values in a rather impressive fashion (Table I). A mean absolute error ($|\overline{x}|$) of only 1.22 kcal/mol was found, and the individual errors themselves show a surprisingly tight distribution around this value (mean absolute deviation, $|\overline{dev}| = 0.76$ kcal/mol).[4] An examination of the maximum absolute errors ($|\max|$) allows the reliability of the method to be assessed. For the G2 procedure, the maximum absolute error is only 5.06 kcal/mol($D_e[SO_2]$).

The G2(MP2,SVP) method of Smith and Radom[1(g)] was developed in an attempt to avoid the most computationally demanding steps of the G2 procedure and yet still retain a very high degree of accuracy.[5] As can be seen in Table I, G2(MP2,SVP) theory offers a performance very similar to that of the G2 procedure. Only modest increases in the above three statistical measures are seen: $|\overline{x}| = 1.63$, $|\overline{dev}| = 1.09$, and $|\max| = 6.14$(IP[S])kcal/mol. These results are especially encouraging given the reduced expense of this approach.

The importance of empirical corrections for both the G2 and G2(MP2,SVP) methods is readily apparent from even a cursory examination of Table II. In the absence of a higher-level correction, the mean absolute error between G2 theory and experiment increases to 4.14 kcal/mol. Moreover, the mean absolute deviation jumps to 2.31 kcal/mol, and the maximum absolute error is 15.47 kcal/mol($D_e[N_2H_4]$). The G2(MP2,SVP) method, stripped of its higher-level correction, yields comparable results: $|\overline{x}| = 4.60$, $|\overline{dev}| = 2.47$, and $|\max| = 17.46$($D_e[N_2H_4]$)kcal/mol. With the exception of proton affinities, for which empirical corrections play no role due to their cancellation, the inclusion of some sort of empirical correction is essential to the success of the G2 and G2(MP2,SVP) methods.

While the current work was inspired by the impressive results of the G2(MP2,SVP) method, it was also motivated by an additional desire: the possible elimination of the empirical correction. The current prescription differs from the G2(MP2,SVP) method in that: (1) the augmented, correlation-consistent basis sets of Dunning *et al.*[6] were

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TABLE I. Fitted (empirically corrected) model chemistries. Mean absolute errors ($|\overline{x}|$) and deviations ($|\overline{\text{dev}}|$) and absolute maximum errors ($|\text{max}|$) for the levels of theory discussed in the text.[a] Statistics are for the full G2 test set (see text for details). Species corresponding to the given value are listed parenthetically. All values are in kcal/mol.

	G2[b]		G2(MP2,SVP)[b]		Current work[c]	
D_e						
$\|\overline{x}\|$	1.18		1.34		3.32	
$\|\overline{\text{dev}}\|$	0.78		0.90		2.33	
$\|\text{max}\|$	5.06	(SO_2)	4.19	(CO_2)	13.82	(SO_2)
IP						
$\|\overline{x}\|$	1.26		1.92		1.70	
$\|\overline{\text{dev}}\|$	0.77		1.19		0.87	
$\|\text{max}\|$	4.37	(Na)	6.14	(S)	5.84	(S)
EA						
$\|\overline{x}\|$	1.31		2.07		1.15	
$\|\overline{\text{dev}}\|$	0.80		1.26		0.83	
$\|\text{max}\|$	3.54	(CN)	4.57	(P)	5.07	(CN)
PA						
$\|\overline{x}\|$	1.01		0.81		1.03	
$\|\overline{\text{dev}}\|$	0.42		0.50		0.41	
$\|\text{max}\|$	2.02	(H_2O)	2.14	(H_2O)	1.77	(HCCH)
Totals						
$\|\overline{x}\|$	1.22		1.63		2.26	
$\|\overline{\text{dev}}\|$	0.76		1.09		1.70	
$\|\text{max}\|$	5.06($D_e[SO_2]$)		6.14(IP[S])		13.82($D_e[SO_2]$)	

[a]See Ref. 4 for statistical definitions.
[b]Values may deviate slightly (in second decimal place) for those reported in original papers due to rounding.
[c]Higher-level correction (HLC) is similar to that of G2(MP2,SVP) theory. See Ref. 14 for statistics associated with the ''G2'' HLC.

TABLE II. Non-fitted (non-empirically corrected) model chemistries. Mean absolute errors ($|\overline{x}|$) and deviations ($|\overline{\text{dev}}|$) and absolute maximum errors ($|\text{max}|$) for the levels of theory discussed in the text.[a] Statistics are for the full G2 test set (see text for details). Species corresponding to the given value are listed parenthetically. All values are in kcal/mol. None of the levels of theory below make any use of a higher-level correction (HLC).

	G2[b]		G2(MP2,SVP)[b]		Current work	
D_e						
$\|\overline{x}\|$	6.07		6.38		2.86	
$\|\overline{\text{dev}}\|$	2.77		3.11		2.02	
$\|\text{max}\|$	15.47	(N_2H_4)	17.46	(N_2H_4)	17.32	(SO_2)
IP						
$\|\overline{x}\|$	2.82		3.33		2.04	
$\|\overline{\text{dev}}\|$	1.04		1.26		1.17	
$\|\text{max}\|$	6.74	(S)	9.36	(S)	7.12	(S)
EA						
$\|\overline{x}\|$	2.80		3.65		1.80	
$\|\overline{\text{dev}}\|$	1.11		1.20		0.90	
$\|\text{max}\|$	5.51	(P)	7.78	(P)	4.38	(P)
PA						
$\|\overline{x}\|$	1.01		0.81		1.03	
$\|\overline{\text{dev}}\|$	0.42		0.50		0.41	
$\|\text{max}\|$	2.02	(H_2O)	2.14	(H_2O)	1.77	(HCCH)
Totals						
$\|\overline{x}\|$	4.14		4.60		2.29	
$\|\overline{\text{dev}}\|$	2.31		2.47		1.48	
$\|\text{max}\|$	15.47($D_e[N_2H_4]$)		17.46($D_e[N_2H_4]$)		17.32($D_e[SO_2]$)	

[a]See Ref. 4 for statistical definitions.
[b]Values may deviate slightly (in second decimal place) for those reported in original papers due to rounding.

used; (2) coupled-cluster (CC)[7] theory was substituted for that of quadratic configuration interaction (QCI);[7(c),8] and (3) all vibrational analyses were carried out at the same level of theory as that of the optimizations. (More detailed descriptions of these differences are provided in footnotes Refs. 10 and 11.) Like the G2(MP2,SVP) procedure, all closed-shell species were treated with restricted wave functions (RHF), and all open-shell systems were described within the unrestricted formalism (UHF).

Optimizations were performed at the MP2/aug-cc-pVDZ level of theory. Zero-point energies (ZPE) were also determined at this level, but the resulting values were scaled by an (empirical) factor of 0.9646.[9] Both sets of calculations made use of the frozen-core (FC) approximation.[10]

Single-point energies were calculated at the following levels: MP2/aug-cc-pVDZ, MP2/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVDZ. In addition to valence electrons, those of the core were also treated explicitly, i.e., the full (FULL) approximation.[11]

The final energy was calculated via Eq. 1, where Δ_{BSC} is the so-called ''basis set extension correction'' and is defined in Eq. 2.

$$\text{E[CCSD(T,FULL)/aug-cc-pVDZ]}+\Delta_{\text{BSC}}+\text{ZPE}, \quad (1)$$

$$\Delta_{\text{BSC}}=\text{E[MP2(FULL)/aug-cc-pVTZ]}-\text{E[MP2(FULL)/aug-cc-pVDZ]}. \quad (2)$$

This scheme approximately corresponds to the CCSD (T,FULL)/aug-cc-pVTZ//MP2(FC)/aug-cc-pVDZ level of theory. With the exception of the coupled-cluster level of theory, all closed-shell calculations were carried out with the GAMESS program.[12] All other computations were performed with the GAUSSIAN 94 suite of programs.[13]

The final column of Table II summarizes the current method's ability to reproduce the 125 experimental values in the test set. *Note that no empirical correction has been employed here.* The mean absolute error (2.29 kcal/mol) is nearly half that found for the G2 method without its higher-level correction (4.14 kcal/mol). Likewise, these errors show less dispersion ($|\overline{dev}|=1.48$ kcal/mol) than for uncorrected (i.e., nonparametrized) G2 model ($|\overline{dev}|=2.31$ kcal/mol). While the maximum absolute error ($D_e[SO_2]=17.32$ kcal/mol) is comparable to that found for the uncorrected G2 method ($D_e[N_2H_4]=15.47$ kcal/mol), it is interesting to note that the next largest error ($D_e[Na_2]$) is only 9.1 kcal/mol. In contrast, uncorrected G2 possesses 11 absolute errors in excess of 9.1 kcal/mol.

Vis-a-vis the uncorrected G2(MP2,SVP) method, the current approach compares even more favorably; the mean

absolute error for the former method (4.60 kcal/mol) is double that found in the present work. The dispersion associated with the uncorrected G2(MP2,SVP) values is also nearly one kcal/mol worse.

If a least-squares fit of the complete G2 test set is performed, *a la* the G2(MP2,SVP) procedure, no significant improvement is obtained (Table I).[14] While the maximum absolute error drops to 13.82 kcal/mol($D_e[SO_2]$), the mean absolute error (2.26 kcal/mol) and mean absolute deviation (1.70 kcal/mol) are virtually unchanged. This result illustrates the highly uncorrelated nature of the present data.

The most significant and, perhaps, surprising comparison is between the results obtained with the *corrected* G2 and G2(MP2,SVP) theories and *uncorrected* current method (Tables I and II, respectively). While the current method is similar in computational cost to the G2(MP2,SVP) procedure, it yields results within the ''appropriate target accuracy'' of G2 theory, i.e., $\pm 2-3$ kcal/mol ($\pm 0.10-0.15$ eV) of experimental error.[1(a),1(b)] But most importantly, the current prescription makes no use of fitted empirical parameters.

Finally, it should be noted that the higher-level correction should take on added importance for systems larger than those of the G2 test set. This is due to the fact that larger systems will possess more spin-paired electrons which in turn will lead to larger correlation energies. As the G2 and G2(MP2,SVP) basis sets are slowly convergent with respect to angular momentum, they can be expected to perform more poorly for larger species. This result has been shown in the literature.[1(j),1(k),1(n)] (Raghavachari *et al.* have shown that cumulative errors accruing from increased molecular size can be minimized with the judicious use of isodesmic reactions[1(i)].) Consequently, model chemistries that make no use of these higher-level corrections warrant further study.

While the current method is potentially useful, it is unreliable at present owing to an unacceptably large range in absolute error. A number of sources for this residual error may be noted: the failure to take account of spin-orbit effects; the necessity to consider explicitly correlation between core and valence electrons; the inadequacy of single determinant wave function descriptions for some species; and, of course, the failure of the additivity assumption itself. The present results are entirely consistent with the beautiful analysis of basis sets and levels of theory by Feller and Peterson,[15] who dramatically illustrate the accuracy one can obtain at the MP2, MP4(SDTQ), and CCSD(T) levels of theory by extrapolating the augmented, correlation-consistent basis sets to the complete basis set (CBS) limit. In the end, the approach advocated by those authors is likely to be quite successful. The above potential sources of error are at present being investigated in our laboratory in hopes of either eliminating them or at least establishing a set of criteria to identify species that are not amenable to the types of model chemistries discussed in this paper.

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[1] (a) J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989); (b) L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **93**, 2537 (1990); (c) L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991); (d) L. A. Curtiss, J. E. Carpenter, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **96**, 9030 (1992); (e) L. A. Curtiss, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **98**, 1293 (1993); (f) A. Nicolaides and L. Radom, J. Phys. Chem. **98**, 3092 (1994); (g) B. Smith and L. Radom, J. Phys. Chem. **99**, 6468 (1995); (h) L. A. Curtiss, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **103**, 4192 (1995); (i) B. J. Smith and L. Radom, Chem. Phys. Lett. **245**, 123 (1995); (j) M. N. Glukhovtsev and S. Laiter, Theor. Chim. Acta **92**, 327 (1995); (k) A. Nicolaides and L. Radom, Mol. Phys. **88**, 759 (1996); (l) L. A. Curtiss, P. C. Redfern, B. J. Smith, and L. Radom, J. Chem. Phys. **104**, 5148 (1996); (m) K. Raghavachari, B. B. Stefanov, and L. A. Curtiss, J. Chem. Phys. **106**, 6764 (1997); (n) L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).

[2] The G2 method is designed to reproduce calculations at the QCISD(T,FULL/6-311+G(3df,2p)//MP2(FC)/6-31G(d) level of theory. (See Ref. 1(c) for details.)

[3] In the G2 prescription, this latter parameter is determined via a statistical fit of the calculated and experimental values for a set of fifty-five dissociation energies. G2(MP2,SVP) theory fits all 125 values of the G2 test set. [See Refs. 1(c) and 1(g), respectively, for details.]

[4] The mean absolute error has been defined as

$$|\overline{x}| = \sum_i \frac{|x_i^{\text{expt.}} - x_i^{\text{calc.}}|}{n}$$

while the mean absolute deviation has been computed via

$$|\overline{dev}| = \sum_i \frac{|x_i^{\text{calc.}} - |\overline{x}|}{n},$$

where $x_i^{\text{expt.}}$ and $x_i^{\text{calc.}}$ are the experimental and calculated values, respectively, and n is the total number of computed values. The maximum absolute error is, of course, the largest term in the numerator of the equation for the mean absolute error.

[5] Specifically, the time-consuming MP4(SDTQ) calculations are eliminated, and the QCISD(T) calculation makes use of the smaller 6-31 G(d) basis set and not that of 6-311G(d,p). [See Ref. 1(g) for details.]

[6] (a) T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989); (b) R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992); (c) D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993); (d) D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **99**, 3730 (1993).

[7] (a) J. Cizek, Adv. Chem. Phys. **14**, 35 (1969); (b) G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982); (c) J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987); (d) G. E. Scuseria, C. L. Janssen, and H. F. Schaefer, III, J. Chem. Phys. **89**, 7382 (1988); (e) G. E. Scuseria and H. F. Schaefer, III, J. Chem. Phys. **90**, 3700 (1989).

[8] (a) J. Gauss and C. Cremer, Chem. Phys. Lett. **150**, 280 (1988); (b) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989).

[9] J. A. Pople, A. P. Scott, M. W. Wong, and L. Radom, Isr. J. Chem. **33**, 345 (1993).

[10] The current computations differ from their G2(MP2,SVP) counterparts in that the latter employed the 6-31G(d) basis set which differs from aug-cc-pVDZ in that polarization and diffuse functions are missing from hydrogen atoms. In the G2(MP2,SVP) method, ZPEs are computed at the Hartree–Fock level of theory.

[11] This set of calculations varies from those carried out at the G2(MP2,SVP) level of theory in the following three ways. The CCSD(T) method has been substituted for that of QCISD(T). The larger aug-cc-pVDZ basis set (see Ref. 10) has been used in both MP2 and CCSD(T) single-point calculations. The G2(MP2,SVP) procedure calls for the 6-31G(d) basis set; it lacks diffuse functions on all atoms and polarization functions on hydrogen atoms. The aug-cc-pVTZ basis set has been employed at the MP2 level. It differs from its G2(MP2,SVP) analog, 6-311+G(3df,2p), in the numbers and types of diffuse and polarization functions used for hydrogen and nonhydrogen atoms.

[12] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, N.

Matsunaga, M. S. Gordon, K. A. Ngugen, S. Su, T. L. Windus, S. T. Elbert, J. Montgomery, and M. Dupuis, J. Comput. Chem. **14**, 1347 (1993).

[13] GAUSSIAN 94, Revision E2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN, Inc., Pittsburgh, PA, 1995.

[14] In the current work, HLC$=-0.00017n_\alpha-0.00203n_\beta$ (n_α and n_β are the number of α and β valence electrons, respectively). If only the fifty-five dissociation energies (D_e) are fit, as in G2(MP2,SVP) theory, then HLC $=-0.00017n_\alpha-0.00182n_\beta$. Using this ''G2'' HLC, the ''current work'' values (all in kcal/mol) of Table I are as follows. D_e: $|\overline{x}|=3.18$; $|\overline{\text{dev}}|=2.27$; $|\text{max}|=14.21(SO_2)$. IP: $|\overline{x}|=1.72$; $|\overline{\text{dev}}|=0.89$; $|\text{max}|=5.98(S)$. EA: $|\overline{x}|=1.18$; $|\overline{\text{dev}}|=0.84$; $|\text{max}|=4.94(CN)$. PA: $|\overline{x}|=1.03$; $|\overline{\text{dev}}|=0.41$; $|\text{max}|=1.77(HCCH)$. Totals: $|\overline{x}|=2.22$; $|\overline{\text{dev}}|=1.68$; $|\text{max}|=14.21(D_e[SO_2])$.

[15] D. Feller and K. A. Peterson, J. Chem. Phys. **108**, 154 (1998).